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SEM-EDS and FTIR Characterization of Aerosols during Diwali and Post Diwali Festival over Delhi: Implications to Human Health

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Abstract

Emission from fireworks is a concern of pollution globally. This degrades the air quality for a small time interval and affects the human health and regional climate. Diwali, known as the festival of lights, is celebrated throughout India every year and the cracker bursting is a major activity in this celebration. To study the physico-chemical characteristics of particles released during this period, particles were collected at National Physical Laboratory (28°38'13'' N, 77°10'14'' E), New Delhi, India during Diwali festival celebrated on November 3, 2013 (Sampling period: October 29 - November 22, 2013). Particles were analyzed for organic functional groups, inorganic species and individual particle physico-chemical properties using FTIR (Fourier Transform Infrared Spectrometer) and SEM-EDS (Scanning Electron Microscope with Energy Dispersive Spectrometer), respectively. Bulk compositional analysis of few samples has been carried out using XRF (X-ray fluorescence spectrometer). Before Diwali, majorly mineral dust particles accompanied with some carbon rich particles with different morphologies were observed. Just after Diwali, zinc rich particle with multi-legged structures together with significant proportions of carbon rich particles sometimes mixed with Pb, K and S were observed based on SEM-EDS analysis. Submicron size (< 0.43 µm) particles were majorly observed to be Cu rich. XRF analysis reveals the dominance of TiO_2, MnO, and CuO just after Diwali (November 4). FTIR analysis reveals the fundamental modes of nitrate, carbonate, silicate, zinc oxide, zinc hydroxide, iron oxide etc. The characteristic bands of CH_2, N–O, C–H, C–O and NO_2 were observed.

Keywords: *Aerosol; FTIR; Health; Morphology; SEM-EDS.*

1. INTRODUCTION

Firecracker bursting is a very common activity which is practiced all around the world as a means to celebrate festivals and happiness. The usage of fireworks varies from a small scale events (like wedding ceremonies and birthday parties etc.) to the large scale celebrations all around the world (like on the annual Guy Fawkes Night in UK, the Spanish Las Fellas festival, the Lantern and Lunar Festival in China and Diwali in India). Diwali is one of the biggest festivals in India celebrated on a national scale**.** From the ancient times to the present day, chemicals (like sulfur, charcoal and potassium nitrate etc.) are being used for the preparation of gunpowder which is major component of fireworks. Aluminum, magnesium together with some chemicals (like ammonium perchlorate, ammonium nitrate, potassium perchlorate, PAHs etc.) are used in the propellant composites for acting as binders, oxidants and fuel in fireworks (Russell, 2009). A number of inorganic and organic constituents are used in the fireworks for generating coloring and sparkling pyrotechnic effects (Russell, 2009). Table 1-2 lists various metals, metallic oxides, organic and inorganic constituents used in the fireworks for various purposes (https://en.wikipedia.org/wiki/Pyrotechnic_composition).

During the bursting of fireworks, these chemical compounds undergo exothermic reactions and as a result, a number of harmful byproducts are formed. Thus the gaseous pollutants (like sulfur dioxide, SO_2;

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carbon dioxide, CO_2; carbon monoxide, CO; oxides of nitrogen, NO_x) and various metallic/non-metallic constituents (like manganese, aluminum, magnesium, lead, zinc, titanium, barium and strontium etc.) are released in the atmosphere due to fireworks which degrade the regional air quality. The heat produced with the burning mixture is managed in such a way that it should be enough to volatilize the organic dyes but not to decompose them as the volatilization of organic dyes gives rise to colored smokes during fireworks. This heat is enough for the vaporization of many compounds but it is not sufficient to decompose them, therefore, these compounds prevail in the air for longer durations. Ravindra *et al.* (2003) reported a significant increase in the concentration levels of SO_2, NO_2, PM_{10} and TSP during Diwali festival over Hisar. The increased PM mass load (Nirmalkar *et al.* 2013; Barman *et al.* 2008; Sarkar *et al.* 2010) with enhanced metal concentrations (Kulshrestha *et al.* 2004; Singh *et al.* 2010) have been reported during Diwali festival. Vijayakumar and Devara (2012) observed the variation in AOD (Aerosol Optical Depth) and reduced visibility due to particulate emissions during the festival. Burning of fireworks is also reported to be associated with the stimulation in the ozone formation as the light emitted from sparkles give rise to dissociation of atmospheric molecular oxygen into atomic oxygen (thus enabling the reaction O_2+O→O_3) (Attri *et al.* 2001). Unusual elevation of the elements like Ti, S, Cl, Mg, K, Sr, Ba, C, Ca, Al, Cu and Pb in the fine mode aerosol were found during various celebration events (Kim *et al.* 2008; Moreno *et al.* 2007; Vecchi *et al.* 2008; Röösli *et al.* 2001; Kulshrestha *et al.* 2004). Amongst the emitted particles, most of the submicron particles have high residence time in atmosphere.

Table 1. Elements and compounds used in the Fireworks as Fuel and Oxidizers.

Elements and compounds used as Fuel	
Metal	Aluminum, Magnesium, Magnalium, Iron, Steel , Zirconium, Titanium, Ferrotitanium, Ferrosilicon, Manganese, Zinc, Copper, Brass
Metal Hydrides	Titanium Hydride, Zirconium Hydride, Aluminum Hydride, Decaborane
Metal Carbides	Zirconium Carbide
Metalloids	Silicon, Boron, Antimony
Non-Metallic Inorganic	Sulfur,Red Phosphorus, White Phosphorus, Calcium Salicide, Antimony Trisulfide, Phosphorus Trisulfide, Calcium Phosphide,Potassium Thiocyanate
Carbon Based	Charcoal, Graphite, Carbon Black, Asphaltum, Wood flour
Organic Chemicals	Sodium Benzoate, Sodium salicylate, Gallic acid, Potassium picrate, Terephthalic acid, Hexamine, Anthracene, Naphthalene, Lactose, Dextrose, Sucrose, Sorbitol, Dextrin, Stearic acid, Hexachloroethane, Polysulfide, Polyurethane, Polyisobutylene, Nitrocellulose, Polyethylene, Polyvinyl chloride, Shellac, Accroides resin
Elements and compounds used as Oxidizers	
Perchlorates	Potassium perchlorate, Ammonium perchlorate
Chlorates	Potassium chlorate, Barium chlorate, Sodium chlorate
Nitrates	Potassium nitrate, Sodium nitrate, Calcium nitrate, Ammonium nitrate, Barium nitrate, Strontium nitrate, Cesiumnitrate
Permanganates	Potassium permanganate, Ammonium permanganate
Chromates	Barium chromate, Lead chromate, Potassium dichromate
Oxides and peroxides	Strontium peroxide, Lead tetroxide, Lead dioxide, Bismuth trioxide, Iron(III) oxide, Iron(II,III) oxide, Manganese(IV) oxide, Chromium(III) oxide, Tin(IV) oxide.
Sulfates	Barium sulfate, Calcium sulfate, Potassium sulfate, Sodium sulfate, Strontium sulfate

Table 2. Additives used in Fireworks

Application	Compound
Coolants	Clay, alumina, silica, magnesium oxide etc.
Flame Suppressants	Potassium nitrate, Potassium sulfate
Opacifiers	Carbon black, graphite
Colorants	Salts of Barium, strontium, calcium, sodium, copper etc. along with chlorine donors.
Catalysts	Ammonium dichromate, iron oxide, manganese dioxide, potassium dichromate, copper chromite, lead salicylate, lead stereate, lead 2-ethylhexoate, copper salicylate, copper stearate, lithium fluoride, n-butyl ferrocene, di-n-butyl ferrocene.
Stabilizers	Carbonates of sodium, calcium or barium, Petroleum jelly, castor oil, linseed oil, etc., organic nitrated amines are used as stabilizers as well, e.g. 2-nitrodiphenylamine.
Anti-caking agents	Fumed silica, magnesium carbonate, graphite etc.
Binders	Gum Arabic, red gum, guar gum, Carboxymethyl cellulose, nitrocellulose, rice starch, shellac, dextrin etc.
Plasticizers	Dioctyl adipate, isodecyl pelargonate,dioctyl phthalate, nitroglycerine, butanetriol trinitrate, dinitrotoluene, trimethylolethane trinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, bis(2,2-dinitropropyl)formal, bis(2,2-dinitropropyl)acetal, 2,2,2-trinitroethyl 2-nitroxyethyl ether
Curing and crosslinking agents	Paraquinone dioxime, toluene-2,4-diisocyanate, tris(1-(2-methyl) aziridinyl) phosphine oxide, N,N,O-tri(1,2-epoxy propyl)-4-aminophenol, andisophorone diisocyanate.
Bonding agents	Tris(1-(2-methyl) azirinidyl) phosphine oxide andtriethanolamine.

A high increase in the mortality rates due to cardiovascular and respiratory diseases has been found to be associated with an increase in the PM concentration (Analitis *et al.* 2006; Anderson *et al.* 2005; COMEAP, 2006; Dockery *et al.* 1993; Dominici *et al.* 2003; Dominici *et al.* 2006; Katsouyanni *et al.* 2003). Respiratory related problems are the function of particle morphology (shape & size) and composition. Toxic metals and organics in the fine mode aerosols cause more serious problems. The excessive exposure to some heavy metals may lead to mental dysfunction and neurological disorders (Kampa *et al.* 2008; Toscano *et al.* 2005). Exposure to metals like Mn and Pb can cause neurodegenerative disorders mimicking Parkinson's, Alzheimer's and Huntington's diseases (Mansouri *et al.* 2009; Bowman *et al.* 2011). Extensive use of fireworks is also expected to raise the black carbon (BC) levels in the air due to the formation of soot (Babu *et al.* 2001). At a faraway distance from the center of fireworks bursting activity, a 3 to 4 fold increase in the levels of BC have been reported during Diwali festival (Babu *et al.* 2001) which indicates the long range transport of firework emissions. BC is supposed to have adverse effects on health by causing pulmonary, respiratory and cardiovascular problems. Also, BC has catalytic properties (Lary *et al.* 1999) and it can act as an active site for catalytic oxidation of SO_2 to sulfates and for the destruction of ozone (Disselkamp *et al.* 2000). The high porosity of BC particles promotes the adsorption of various particles and compounds from air and it can act like a carrier of harmful and toxic compounds to the pulmonary system.

Till date, most of the studies on pollution emission during Diwali festival are limited to the bulk chemical analysis of the samples but present study deals with the detailed morphological and compositional analysis of individual particles. Here, we also report the FTIR analysis of the samples to trace the signatures of various organic and inorganic species emitted during the festival. In this paper, we have characterized aerosols collected pre and post Diwali festival in Delhi. The particles collected during this period have been analyzed using various analytical techniques: SEM-EDS for individual particle morphology and chemical composition analysis; FTIR for functional group analysis, XRF for bulk chemical composition analysis of few samples. Meteorological parameters (temperature, humidity and wind velocity) have also been observed during the experiment.

2. STUDY AREA

Delhi is the capital and one of the major states of India having a population above 22 million. The state spreads over 1483 square kilometers of area and it is situated at the center of the Indian subcontinent (*UN World Urbanization Prospects: The 2014 Revision*). The state lies in the northern part of India. Due to the large population residing in Delhi, the impact of any

anthropogenic activity (like bursting of fireworks on Diwali) is considerable and acute. Particulate sampling was carried out at a height of approximately 12 m above the ground level on the terrace of the TEC building (site A) at the CSIR-National Physical Laboratory, NPL (28°38′13″ N, 77°10′14″ E) located in New Delhi (fig. 1). The NPL campus is located in the center of Delhi where a large population resides all around. The influence of the Traffic is also expected due to close proximity of the sampling site to the Dr. K. S. Krishnan road. To better understand the impact of firework emissions on the air quality of Delhi, we have performed PM_5 particulate sampling from Oct. 29 - Nov. 22, 2013 including the date of Diwali celebration (Nov. 3, 2013).

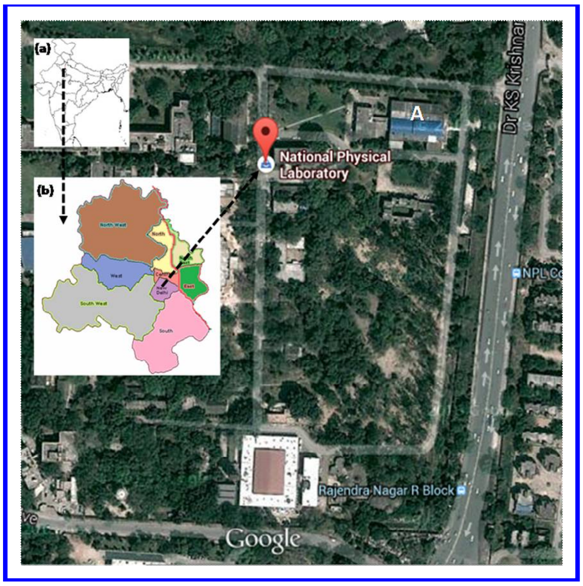

Fig. 1: Sampling Site *A* at the National Physical Laboratory. Inset (a) shows map of India while inset (b) shows the map of Delhi

3. SAMPLING PROCEDURE

The aerosol sampling has been done with the help of a battery operated handheld sampler (Model: Envirotech APM 801) to collect PM_5 particles on the 37mm PTFE filters. The air flow rate of the sampler was generally kept at 2.0 L/min (LPM). Sampling has been carried out between 10:30 to 16:30 hrs local time from 29 October - 22 November, 2013. Together with PM_5, fine particles were also collected during Diwali day using Anderson sampler. For carrying out the SEM-EDS analysis, a segment of a thin foil of tin is utilized as collection substrate and was positioned above the PTFE filter during the sampling. To avoid the over-deposition, low flow rate sampler was used with tin substrate exposed for less time (~ 2 hr). The PTFE filters were analyzed with the FTIR spectroscopy for the detection of a variety of organic and inorganic compounds. Few filters were used for XRF analysis to study the bulk chemical compositions. Here, it is noteworthy to mention that XRF and FTIR are non-destructive techniques.

4. CHARACTERIZATION TECHNIQUES

4.1 SEM-EDS

The surface morphologies and individual particle elemental chemical composition were studied using a Scanning Electron Microscope (SEM: ZEISS EVO MA-10) equipped with an energy dispersive spectrometer (EDS: Oxford Link ISIS 300) facility. SEM is capable of resolving 3nm size particle at 30KV accelerating voltage. Energy dispersive spectrometer attached to the SEM can identify the elements having atomic numbers of the elements from beryllium (Be) to uranium (U) with an accuracy of 133eV.

4.2 FTIR

FTIR is very old and commonly used technique for identifying organic functional groups and inorganic species to study the molecular structure and chemical bonding. FTIR spectroscopy can be applied to study solids, liquids and gaseous samples. This is a powerful tool for qualitative and quantitative (on availability of standards) estimation of various species. The main advantage of FTIR spectroscopy is its non-destructive sample analysis especially useful for aerosol samples which are to be used for different analysis.

For identifying the organic and inorganic species, FTIR (Model: IFS 125M from Bruker) was used. The absorbance spectra of PTFE filters (blank and exposed filters) were recorded at 4 cm^{-1} resolution with 64 scans and wave number range, 500-4000 cm^{-1}. The spectra of the blank filter (without exposure; before particle collection on filter) with the background was used to remove the effect of filter and medium from that of exposed filters (with exposure; particles collected on filter) to understand the characteristics of collected aerosols. Mercury Cadmium Telluride, MCT (420-12000 cm^{-1}) detector, KBr beam splitter and MIR source (450-4800 cm^{-1}) were used for the recording of the IR spectra.

4.3 XRF

Energy Dispersive X-ray Fluorescence (EDXRF) (model no: Epsilon5; PANalytical Instruments Netherland) was used for the bulk compositional analysis. This is a unique high-resolution fully integrated XRF spectrometer combined with advanced elemental excitation capabilities with sophisticated instrument control and analytical software. The

instrument has a combination of optimized Cartesian-geometrical design for lower backgrounds and extended K line excitation 100 kV X-ray capability technology. Aerosol samples collected on PTFE filters for two different dates have been analyzed using this technique.

5. RESULTS & DISCUSSION

5.1 Individual particle characterization by SEM-EDS

Particles with different morphologies and composition were traced. To study the change in physico-chemical properties of particles in the pre and post Diwali event, aerosol samples collected before and after the Diwali event have been analyzed using SEM-EDS and shown in figs. 2-5. Here, the approach of the study is a comparative analysis of the particles prevailing in the atmosphere before and after Diwali event and identification of the changes in particle's elemental composition. Fig. 2 shows the particle SEM images along with their chemical composition based on the spot EDS spectrum for some of the particles collected before Diwali Festival. Fig. 2a shows the carbonaceous particle with spherical shape with diameter ~ 9µm. Figs. 2b and 2c show the super micron size non-spherical dust particles. Some super micron size non-spherical particles were observed to be rich in aluminium oxides, flaky carbon and Ca. Thus, before Diwali, we observed majorly mineral dust particles (sometimes rich in Al and Ca) accompanied with some carbon rich particles with different morphology. The carbonaceous particles before Diwali may have originated due to anthropogenic activities like biomass burning, vehicular emissions etc. A noticeable high percentage of aluminum was found for the particles collected two days before Diwali. This might be due to some localized pre-Diwali fireworks bursting. However, here it is difficult to quantify the amount of Ca and Al contributed due to mineral dust and fireworks. Figs. 3a, 3b and 3c show the C rich particle, mineral dust particle and gypsum particles, respectively during the Diwali day.

Fig. 4 show the morphology and composition of individual particles collected after Diwali festival. Here, it is noteworthy to mention that in the fireworks, metals are generally used as fuels and for creating sparkling effects. Pure carbonates and sulfates of calcium are used to produce reddish orange color in the cracker lights (Russell, 2009).

Fig. 4a shows the zinc rich particle. Multi-legged structures have been observed to be adhered on this particle. These multi-legged structures can be expected to be Tetrapods of ZnO. Zinc oxide tetrapods are the structures having four cylindrical ZnO nanowires connected together at a tetrahedral core (Newton and Warburton, 2007). Natural existence of these tetrapods is difficult to explain as it requires very high temperature (>700 ^{o}C) for their formation (Newton and Warburton, 2007). A high temperature synthesis of ZnO tetrapods in the presence of oxygen has been illustrated by Wang *et al.* (Wang *et al.* 2005). They prepared ZnO tetrapods by rapidly heating Zn powder in air in the presence of oxygen. Occurrence of such particles in the collected sample can be associated with the fireworks bursting. Use of zinc powder in some smoke compositions, rocket fuels and also in pyrotechnic stars give rise to formation of aforementioned ZnO structures at high temperature (1000 to 1600 ^{o}C) during firework burst (Russell, 2009). Fig. 4b shows carbon rich rectangular particles with traces of Na, Mg, Al, Si, K, S, Ca and Fe while Fig. 4c shows particle rich in Ca oxide.

Particles rich in carbon and oxygen sometimes followed with Pb, K and S. Lead is highly toxic element which can cause both chronic and acute effects on health like neurological, cardiovascular, renal, gastrointestinal, haematological and reproductive effects (Airas *et al.* 2004; Al Khayat *et al.* 1997; Apostili *et al.* 2000; Bellinger *et al.* 2005). One of the most critical effects of lead exposure is the neuro-developmental effects on children, even at lower exposure levels (Bellinger *et al.* 1994; Belinger *et al.* 1992). The carbon rich particles would have been released in the atmosphere due to fireworks. Dust particles, carbon particles with fractal morphology, particles rich in carbon and oxides of Al and Si were also observed along with 1 micron radius spherical dust particle and super-micron size carbon fractal adhered to the dust particle.

A significant amount of carbon particles were observed in the post Diwali samples. These particles were observed to be of different morphology. Some of the particles were observed in the fractal shape comprising of carbon spherules (spherules formed of graphitic sheets; whole particle referred as elemental carbon, EC) while others were observed in form of aggregate rich in carbon. Soot which is referred as complex mixture of EC and highly polymerized organic substances has been reported to show several adverse health effects after exposure (Summerhays *et al.* 1991; Oberdörster *et al.* 1990). EC is the dominant light absorbing component among the carbonaceous aerosols and thus plays an important role in governing the regional radiation budget. The fractal carbon is supposed to have a large surface to volume ratio which alters its optical properties compared to that of equivalent sphere when interacting with the incoming solar radiation.

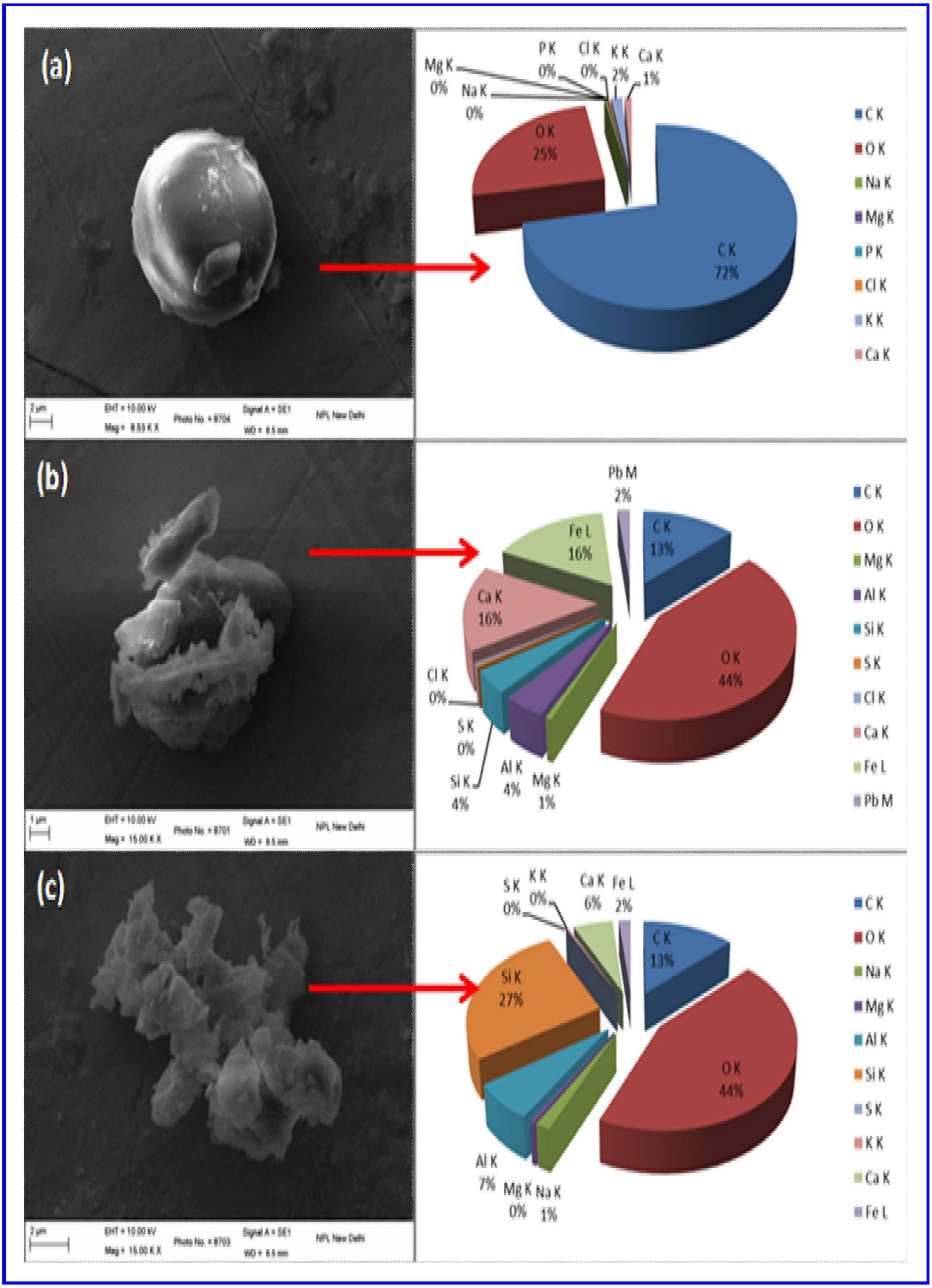

Fig. 2: Micrograph and respective elemental composition of individual particles collected on 29/10/2013 before Diwali event. K, L and M after the element's symbol represent the x-rays which are coming from K, L and M shell energy levels of respective element.

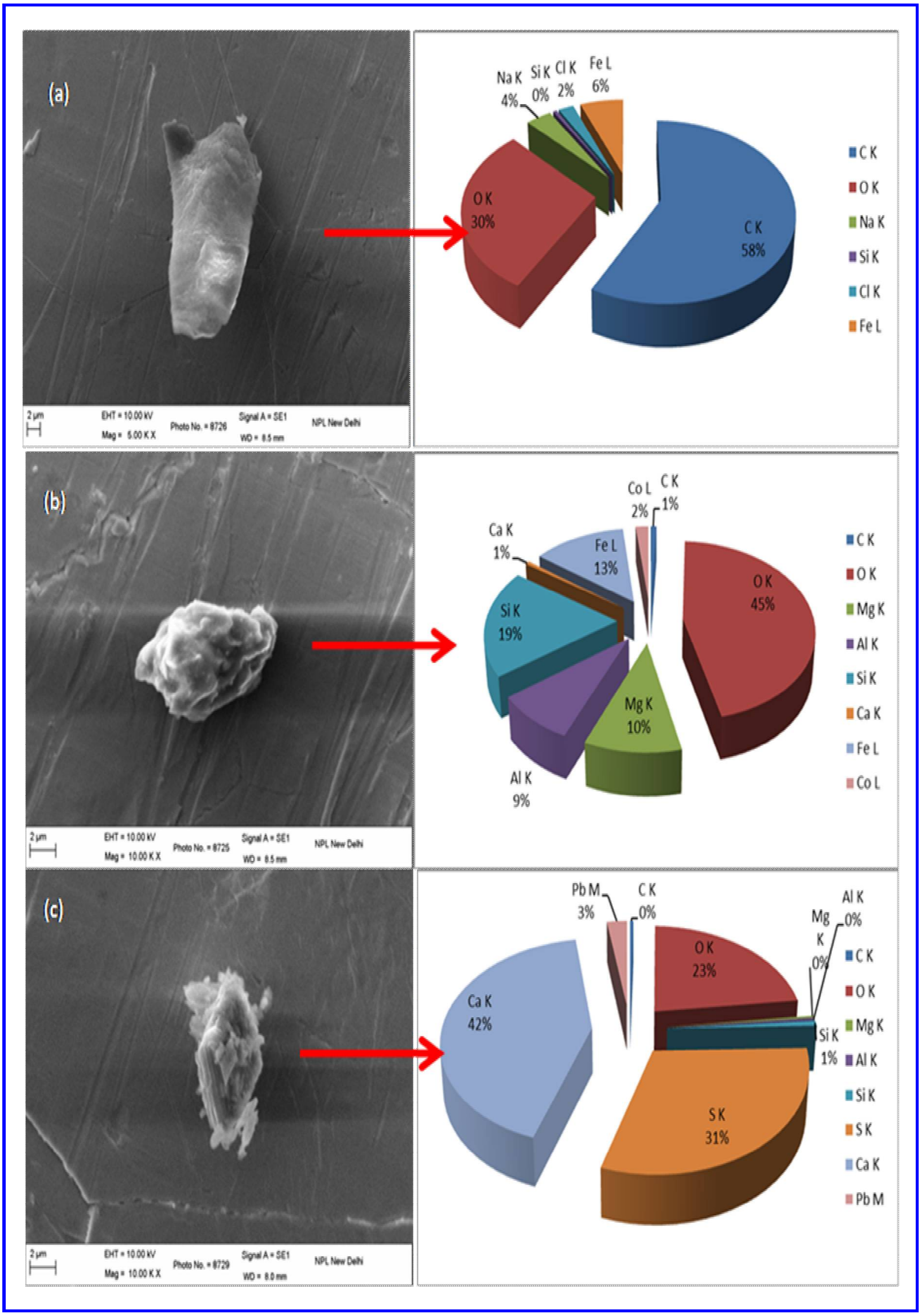

Fig. 3: Same as figure 2 but for particles collected on 03/11/2013 during Diwali event.

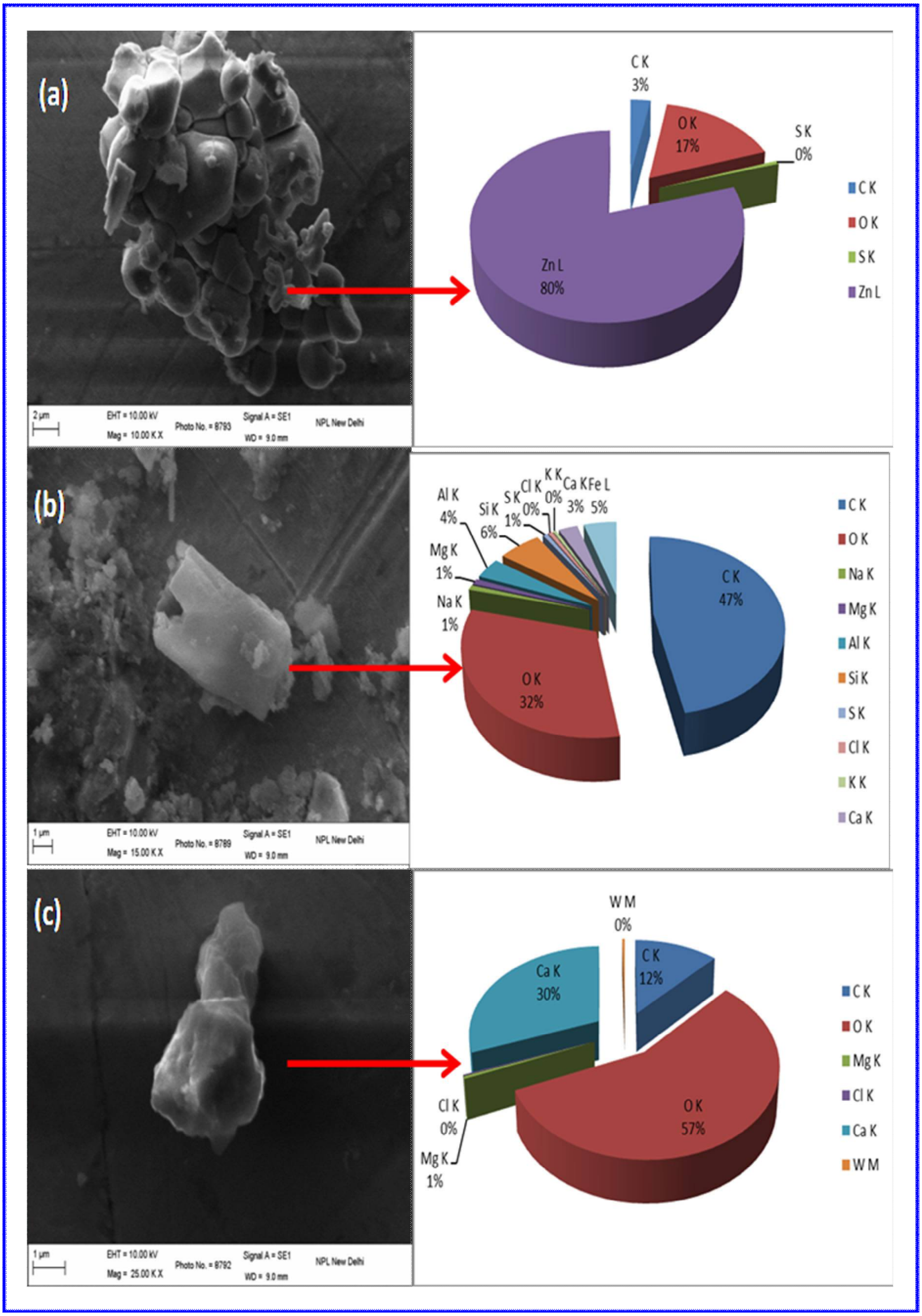

Fig. 4: Same as fig. 2 but for particles collected on 04/11/2013 after Diwali event.

Fig. 5 shows the SEM-EDS of submicron (< 0.43 um) particles collected during Diwali (03-05 Nov, 2013) using Anderson sampler. Figs. 5a and 5b show the abundance of Cu rich particles while Fig. 5c shows the particles rich in oxides of Al and Ca.

5.2 Bulk Particle Characterization

5.2.1 XRF

Aerosol samples collected on PTFE filters for November 4 (just after Diwali) and November 21 (many days after Diwali) have been analyzed for chemical composition of non-carbonaceous species using XRF analysis. The departure in weight percentage of the observed aerosol constituents on November 21 relative to that of November 4 has been shown in Fig. 6. TiO_2, MnO and CuO were observed to be completely absent on 21st while oxides of Ca, K and S were found to be reduced compared to that of 4th November. Aluminum oxides (Al_2O_3), quartz (SiO_2), hematite (Fe_2O_3) and Cl were found comparatively more in November 21st sample. The Cl concentration has been observed to be higher on a post Diwali day (21st Nov) compared to that of during Diwali. A recent study by Kumar *et al.* (2015) over the same sampling site tells about the abundance of Cl in the background conditions due to open-waste burning activities. There could have been excessive open-waste burning activity during that day. Titanium metal is used in firework to produce silver sparks while Cu is used to generate blue color.

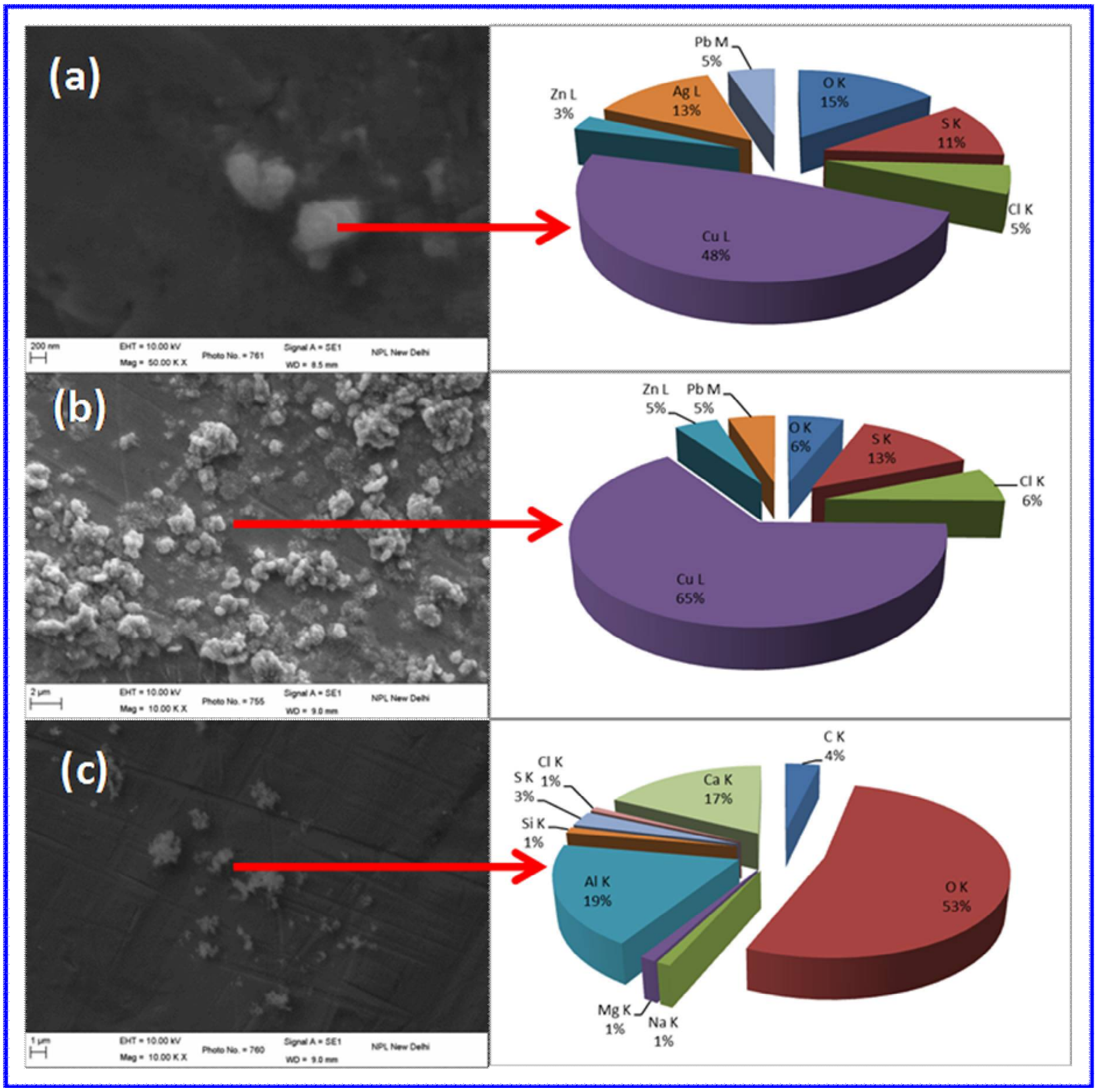

Fig. 5: Same as fig. 2 but for sub-micron particles collected during Diwali event using Anderson sampler

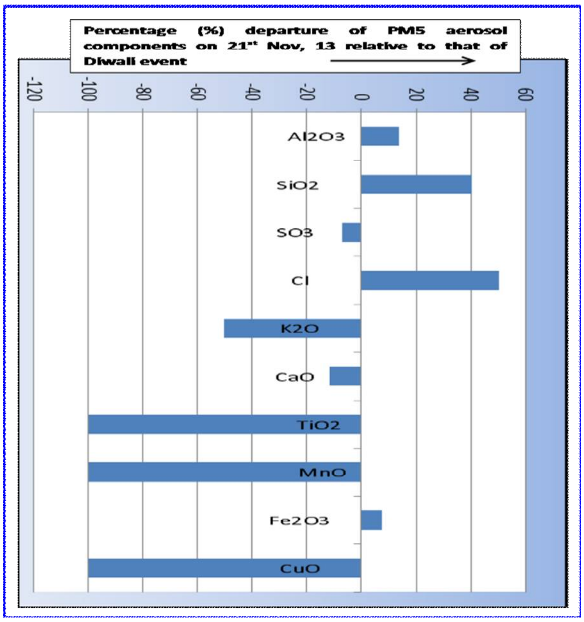

Fig. 6: Weight percentage departure of non-carbonaceous species on 21st Nov, 13 relative to that of 4st Nov, 13 (next day of Diwali event). Bulk composition study has been carried out based on XRF analysis.

5.2.2 FTIR

Fig. 7 shows the FTIR spectra of post Diwali aerosols collected from 4-22, November, 2013. IR absorbance spectra were recorded in 4000–500 cm^{-1} region at ambient temperature. The spectra of aerosol samples were very complex as compared to that of homogeneous engineered aerosol sample. The aerosol which is generated artificially in the lab is termed as engineered aerosol. Diwali is one of most extensively celebrated festival of India. During this period, lots of crackers and fireworks are exploded which increase pollution level in the atmosphere by forming many toxic and hazardous stable inorganics (nitrates, carbonates, and phosphates), organic compounds and gases in the atmosphere. The aforesaid constituents are the outcome of the cracker decompositions at higher temperatures. By considering this fireworks background, Infrared absorption spectra were analyzed and the peaks are assigned based on the earlier reported work on fireworks (Castro *et al.* 2011). Infrared antisymmetric stretching and symmetric stretching fundamental modes of water, amines and silicates are observed in 3600-3000 cm^{-1} region as broad absorption band (Herzberg, 1947; Silverstein *et al.* 1976; Stuart, 2004; Wilson *et al.* 1955). The broadness of the band is attributed to presence of hydrogen bonding in the system. IR technique is very sensitive to the detection of water. The sensitive IR technique can detect water/moisture content at ppm or even ppb levels. Aerosols may adsorb moisture from atmosphere and form hydrated layer around them which may not be completely removed after proper purging of the instrument. In general, almost all hygroscopic particles possess hydrated water in normal humid conditions. IR absorption spectra (fig. 7) showed fundamental vibration modes of nitrate, carbonate, silicate, zinc oxide, zinc hydroxide, iron oxide etc. IR absorption spectrum is dominated by the aluminosilicate and amino group anti-symmetric and symmetric stretching modes in the region 3600 – 3000 cm^{-1} region with peak maximum at ~ 3347 cm^{-1} in 4 Nov. (just after Diwali). These signatures are not observed for other day's spectrum. The presence of these modes confirms the presence of moisture, aluminosilicate mineral and amino compounds in the atmosphere. Methylene (CH_2) group present in aliphatic chain and methyl group stretching, scissoring and wagging modes are observed as strong absorption bands with maxima at 2960 cm^{-1}, 1457 cm^{-1} (CH_2 scissoring), 1377 cm^{-1} (C–H scissoring), 1305 cm^{-1} (CH_2 wagging) and 972 (C–H scissoring) in 4th Nov. IR absorption spectrum whose intensity drastically reduced in 5th Nov. spectrum and again reappears in 6th Nov. onward spectra. The intensity of this peak increases till 13th Nov. and then it again starts decreasing. The presence of these peaks in spectra showed the formation of various saturated and unsaturated organic compounds during post Dewali period which would have disintegrated with time due to photocatalytic reaction initiated by UV radiation. The N-O stretching mode of nitrocellulose/strontium nitrate/aluminosilicate/aldehydes/ketones/aromatics are observed at 1636 cm^{-1} only in 4th Nov. spectrum as a medium intensity peak which was found to disappear in the later spectra. This peak has already been reported for nitrocellulose and strontium nitrate (Castro *et al.* 2011) but at this position aluminosilicate, aldehydes, ketones and aromatics modes also appear. This is the reason why the assignment has been attributed to all these compounds. It has already been discussed that potassium, barium and strontium salts are generally used in crackers to produce color during ignition. The barium nitrate and strontium nitrate salts are produced by the exothermic chemical reaction between their oxide and nitro/amino organic compounds which are used to produce explosive sound. The stability of barium nitrate is highest in dry oxygen atmosphere and slightly less under humid oxygen rich atmosphere (Tronconi and Groppi, 2000; Cybulski and Moulijn, 2005). The nitrate/nitro groups present in Potassium nitrate/barium nitrate/strontium nitrate/pyranose showed peaks at 1384 cm^{-1}, 1359 cm^{-1}, 1247 cm^{-1} (N–O symmetric stretching of NO_3^-), 807 cm^{-1} (N–O–N bending of NO_3^- group), 786 cm^{-1}, 716 cm^{-1} (NO_2 wagging), 690 cm^{-1} (pyranose), 658 cm^{-1} and 645 cm^{-1} (NO_2 rocking) and 542 cm^{-1} (pyranose). IR bands due to ammonium perchlorate were observed at 3161, 1399, 1142, 1120, 1108, 1086, 940, 839, 749 and 626

cm-1; barium nitrate at 1359, 807, 786 cm^{-1}; and nitrocellulose at 1636, 1242 cm^{-1}, 1208, 1150, 1101, 1044 and 998 cm^{-1}. The bands at 2937, 2837, 1457, 1274 and 998 cm^{-1} matches with that of shellac, an organic resinous compound. IR spectra also showed the presence of alumino-silicate mineral peaks at 3649, 1636, 1101, 1044, 997, 716, 690, 537, and 490 cm^{-1}. The presence of zinc oxide was also traced by the appearance of Zn-O stretching mode at 572 cm^{-1}; however, tetrapods of ZnO have already been observed and discussed in earlier section based on SEM-EDS analysis. Based on the overlapping possibilities of various organic and inorganic species, all the probabilities have been considered and the assignments were made on the broad basis. Actually during firework cracking periods, lots of organic and inorganic species are available in the active state i.e. in radical or ionic form in the atmosphere. These species may react with each other to form further stable compounds. This FTIR analysis has given some insights regarding the formation of many organic and inorganic compounds resulting due to lots of simultaneous disintegration and formation reactions in the atmosphere during/after cracker bursting.

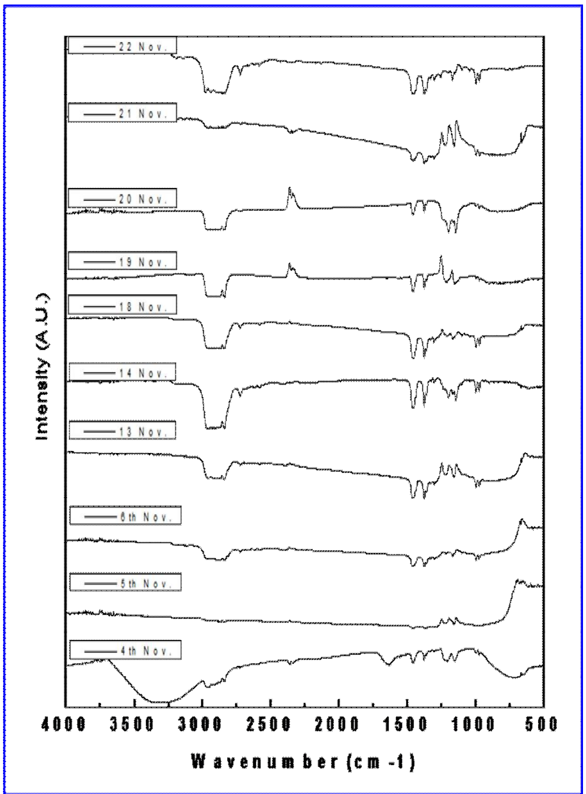

Fig. 7: FTIR spectra of post Diwali aerosols. Dates of aerosol sample collection have also been shown

5.3 Meteorological conditions

Figs. 8, 9 and 10 show the temporal variation of meteorological parameters. Fig. 8 shows the temporal variation of temperature for the study period at three different heights (≤32 m; 2, 20 and 32m shown in three different colors). From 29th October - to 2nd November (before Diwali festival), the average maximum temperature was ~30 ° C for all altitudes (except on 2nd Nov.) while minimum was observed to be ~15° C for 2m altitude. From Nov. 3 – 22 (Diwali and post Diwali festival), the maximum temperature range was 25-30 °C while minimum temperature range was observed to be 10-15 °C. The temperature reduction over the sampling site after Diwali festival may be due to attenuation of incoming solar radiation by the enhanced concentration of suspended aerosols in air medium which were generated due to huge fireworks.

Fig. 9 shows the temporal variation of RH (%) for the study period at heights discussed earlier. For the considered period, the humidity was within the 20-90 %. No remarkable variation due to Diwali festival could be observed.

Fig. 10 shows the temporal variation of wind velocity (m/s) for the study period. Throughout the period the wind was nearly calm and sometimes prevalence of light air was observed. Thus, this condition will give rise to less ventilation of particles generated due to fireworks during Diwali.

5.4. Implications to human health

The fireworks burst leads to the emission of several toxic elements which cause a number of adverse effects on the human health. The rise in the level of metals like Ti, Mn, and Cu just after Diwali (fig. 6) can have acute effects on human health. It has already been discussed that in fireworks, Titanium metal is used to produce silver sparks; Mn to produce green, pink sparkles and Cu to generate blue color.

The exposure of Titanium oxide nano particles to adult mice has been found to induce emphysema and lung redness. Also, its exposure to the developing lungs may lead to chronic irritation and negative effect on lung development with an increased risk of respiratory disorders (Ambalavanan *et al.* 2012). International Agency for Research on Cancer and the National Institute for Occupational Safety and Health declared Titanium as "possible carcinogenic to humans". Titanium dioxide causes adverse effects to health by producing oxidative stress, causing cell damage, redness, and affecting immune response (Skocaj *et al.* 2011). Its exposure may also be harmful to brain. After inhalation through the nose and olfactory bulb, these particles enter directly into the hippocampus region of the brain and show their toxic effect on glial cells resulting in brain injury (Márquez-Ramírez *et al.* 2012).

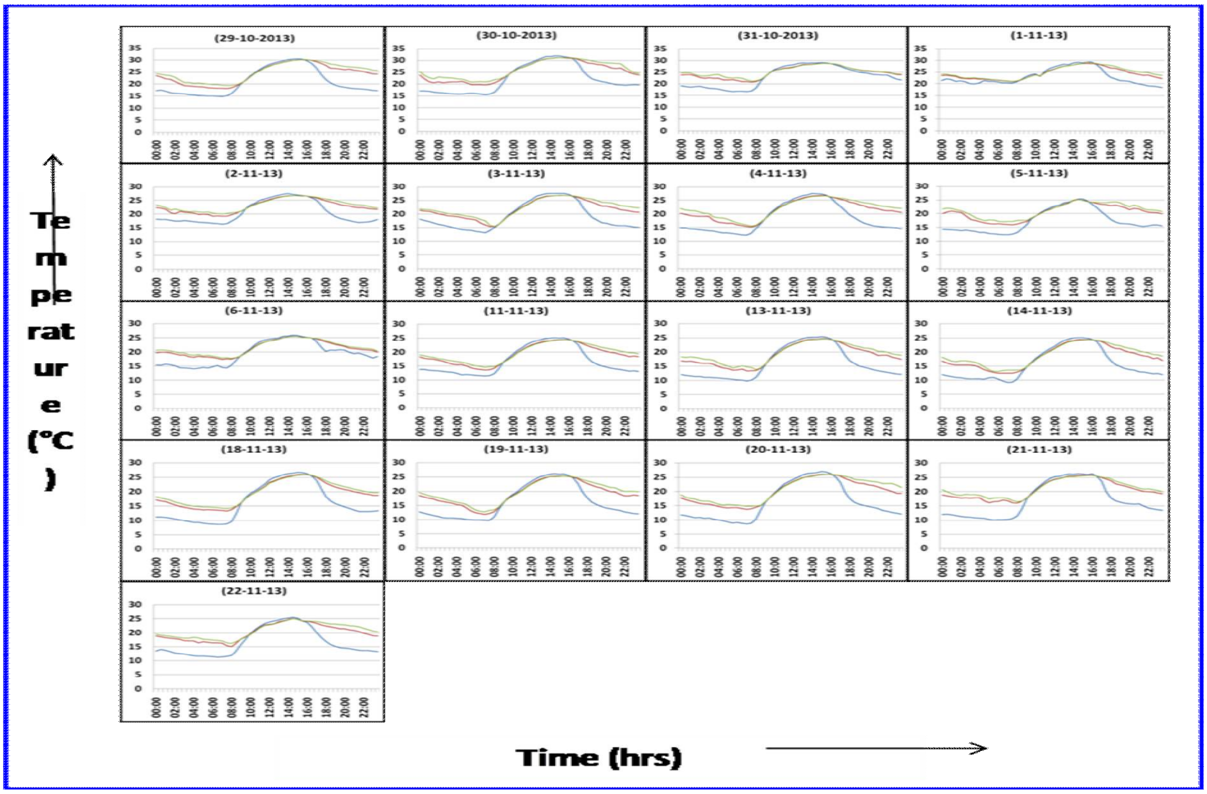

Fig. 8: Temporal variation of temperature for the study period at three different heights (≤32 m; shown in three different colors)

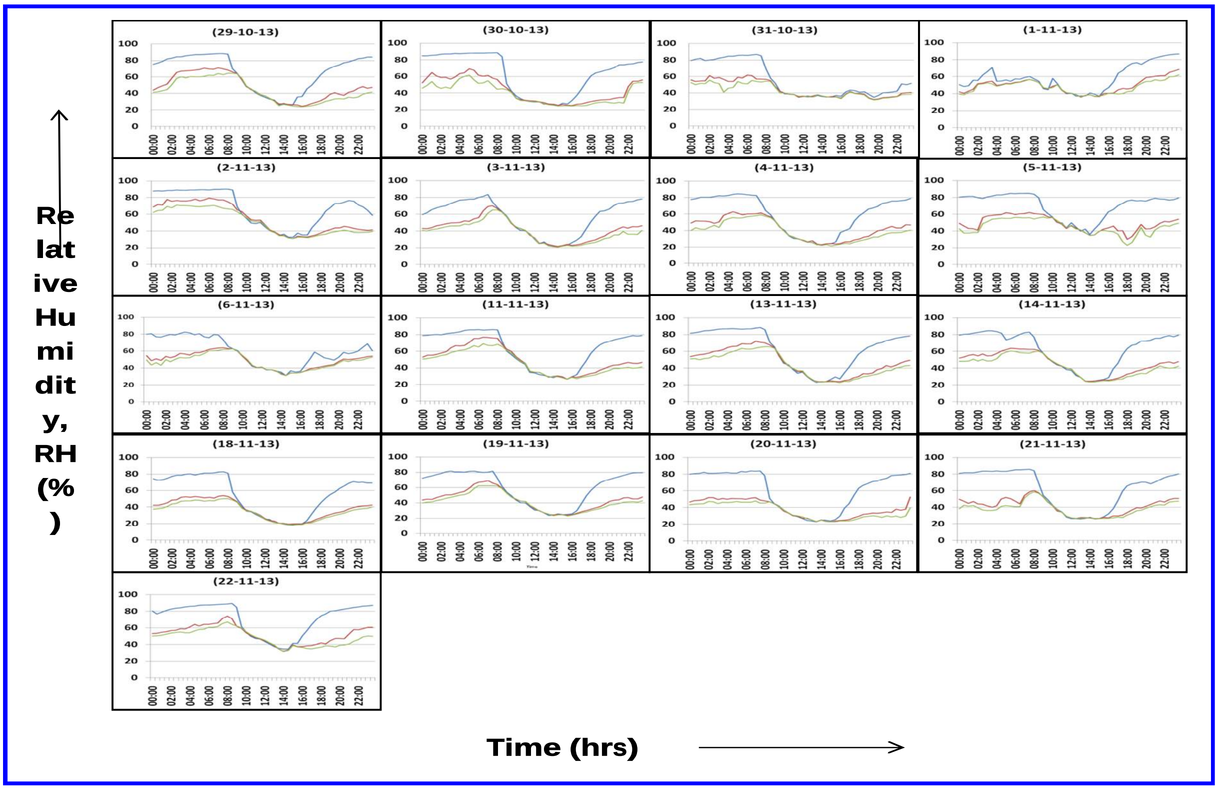

Fig. 9: Same as figure 8 but for RH (%)

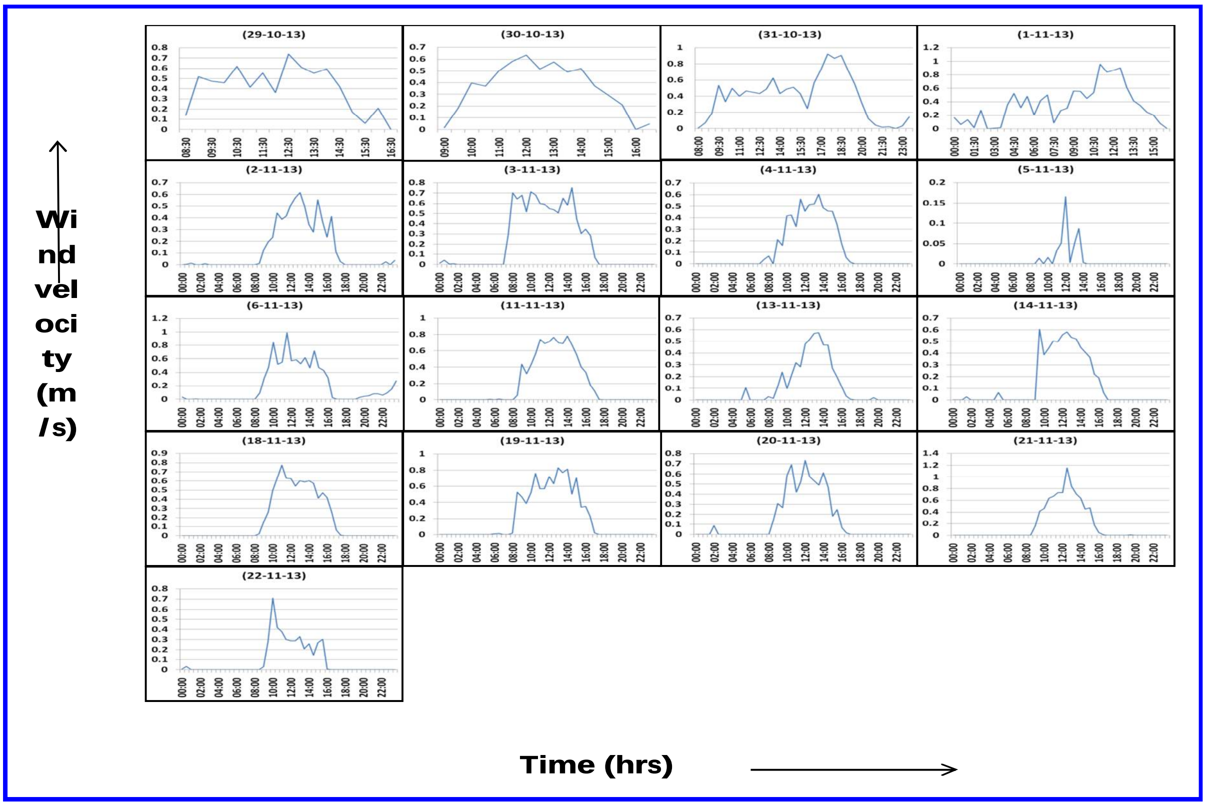

Fig. 10: Same as figure 8 but for wind velocity (m/s)

The exposure to high manganese levels is toxic to human health (*Agency for Toxic Substances and Disease Registry*; http://www.atsdr.cdc.gov/ToxProfiles/tp151-c1-b.pdf). In general, the inhaled manganese is transported directly to the brain before getting metabolized by the liver. This may result in a permanent neurological disorder where tremors, difficult walking, and facial muscle spasms act as indicator of the disease. Intermediate to acute Mn exposure also affects the respiratory system and give rise to an increased susceptibility to infections such as bronchitis and can also cause manganic pneumonia (*Agency for Toxic Substances and Disease Registry*; http://www.atsdr.cdc.gov/toxprofiles/tp151-c2.pdf).

Cu particles have been reported irritating to the respiratory tract. Coughing, sneezing, runny nose, pulmonary fibrosis, and increased vascularity of the nasal mucosa have been reported in workers exposed to copper dust (*US department of health and human services*; http://www.cdc.gov/niosh/docs/81-123/pdfs/0150.pdf).

Fireworks also emit harmful gases like sulfur and nitrogen oxides which are highly toxic and increase the risk of Sudden Infant Death Syndrome (SIDS) (Dales *et al.* 2004). The emission of potassium and ammonium perchlorates can contaminate the soil and water resources which also give rise to thyroid problems (Fireworks, 2015). The emission of large numbers of soot particles due to fireworks may also cause irritation to respiratory system. The submicron soot particles have been linked to tens of thousands of premature deaths every year. It is also associated with increased emergency room visits, asthma attacks, decreased lung function and other respiratory problems (Frampton *et al.* 2004).

6. CONCLUSION

The change in regional air quality due to firework emission is of major concern for human health and climate. The Diwali festival is known as the festival of lights in India and is celebrated throughout the country every year. As the cracker bursting is a major activity after the festival, the chemical characterization of thus emitted particles at bulk and individual particle level is very important to understand their possible effects on human health and regional climate.

Atmospheric particles were collected at National Physical Laboratory (28°38′13″ N, 77°10′14″ E), New Delhi, India during Diwali festival using hand held sampler. Particles were analyzed using various analytical techniques. Based on individual particle SEM-EDS analysis, majorly mineral dust particles

were traced before Diwali while zinc and carbon rich particles were observed just after Diwali. Oxides of Ti, Mn and Cu were found to be abundant just after Diwali based on XRF analysis. FTIR analysis provided qualitative information of various organic and inorganic species. The observation reveals that the fireworks during the festival give rise to many toxic particulates which are dangerous to human health.

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REFERENCES

Airas, S., Duinker, A. and Julshamn, K., Copper, Zinc, Arsenic, Cadmium, Mercury and Lead in *Blue mussels* (*Mytilusedulis*) in the Bergen Harbor area, Western Norway, *Bulletin of Environmental contamination and toxicology*, 73(2), 276-284(2004).
doi: 10.1007/s00128-004-0424-y

Al Khayat, A., Menon, N. S. and Alidina, M. R.,. Acute lead encephalopathy in early infancy clinical presentation and outcome, *Ann Trop Paediatr.*, 17 (1), 39-44(1997).

Ambalavanan, N., Stanishevsky, A., Bulger, A., Halloran, B., Steele, C., Vohra, Y. and Matalon, S., Titanium oxide nanoparticle instillation induces inflammation and inhibits lung development in mice, *Am. J. Physiol. Lung Cell Mol. Physiol.*, 304(3), L152-161(2013).
doi:10.1152/ajplung.00013.2012.Epub 2012 Dec 7

Analitis, A., Katsouyanni, K., Dimakopoulou, E., Samoli, A. K., Nikoloulopoulos, Y., Petasakis, G., Touloumi, J., Schwartz, H., Anderson, H. R., Cambra, K., Forastiere, F., Zmirou, D., Vonk, J. M., Clancy, L., Kriz, B., Bobvos, J. and Pekkanen, J., Short-term effects of ambient particles on cardiovascular and respiratory mortality, *Epidemiol.*, 17(2), 230-233(2006).
doi:10.1097/01.ede.0000199439.57655.6b

Anderson, H. R., Atkinson, R. W., Peacock, J. L., Sweeting, M. J. and Marston, L., Ambient particulate matter and health effects: publication bias in studies of short-term associations, *Epidemiol.*, 16(2), 155-163(2005).

Apostili, P., Bellini, A., Porru, S., Bisanti, L., The effect of lead on male fertility: a time to pregnancy (TTP) study, *Am. J. Ind. Med.*, 38, 310-315(2000).

Attri, A. K., Kumar, U. and Jain, V. K., Formation of Ozone by Fireworks, *Nature*, 411, 1015(2001).

Babu, S. S. and Moorthy, K. K., Anthropogenic impact on aerosol black carbon mass concentration at a tropical coastal station: A case study, *Current Science*, 81(9), 1208-1214(2001).

Barman, S. C., Singh, R., Negi, M. P. S. and Bhargava, S. K., Ambient air quality of Lucknow City (India) during use of fireworks on Diwali Festival, *Environ. Monit. Assess.*, 137, 495-504(2008).

Bellinger, D., Stiles, K. and Needelman, H. L., Low-level exposure, intelligence and academic achievements: A long-term follow-up study, *Paediatrics.*, 90(6), 855-861(1992).

Bellinger, D., Leviton, A., Allered, E. and Rabinowitz, M., Pre- and postnatal exposure and behaviour problems in school-aged children, *Environmental Research.*, 66, 12-30(1994).

Bellinger, D., Teratogen update: Lead and pregnancy, *Birth Defects Res. A Clin. Mol. Teratol.*, 73(6), 409-420(2005).

Bowman, A. B., Kwakye, G. F., Hernandez, E. H. and Aschner, M., Role of manganese in neurodegenerative diseases, *J. Trace. Elem. Med. Biol.*, 25, 191-203(2011).

Castro, K., de Vallejuelo, S. F.-O., Astondoa, I., Goni, F. M. and Madariaga, J. M., Analysis of confiscated fireworks using Raman spectroscopy assisted with SEM-EDS and FTIR, *J. Raman Spectroscopy.*, 42, 2000-2005(2011).

COMEAP, 2006. A Report by the Committee on the Medical Effects of Air Pollutant's Cardiovascular Sub-Group. Cardiovascular Disease and Air Pollution. United Kingdom Department of Health, London, United Kingdom, 208 pp.

Cybulski, A. and Moulijn, J. A., Structured Catalysts and Reactors, Second Edition, Taylor and Francis, (2005).

Dales, R., Air pollution and sudden infant death syndrome, *Pediatrics.*, 113 (6), e628-e631(2004).

Disselkamp, R. S., Carpenter, M. A., Cowin, J. P., Berkowitz, C. M., Chapman, E. G., Zaveri, R. A. and Laulainen, N. S., *J. Geophys. Res.*, 105, 9767–9771(2000).

Dockery, D., Pope, C., Xu, X., Spengler, J., Ware, J., Fay, M., Ferris, B. and Speizer, F., An association between air pollution and mortality in six U. S. cities, *N. Engl. J. Med.*, 329, 1753-1759(1993).

Dominici, F., McDermott, A., Zeger, S. L. and Samet, J. M., National maps of the effects of particulate matter on mortality: Exploring geographical variation, *Environ. Health Perspect.*, 111, 39-43(2003).

Dominici, F., Peng, R. D., Bell, M. L., Pham, L., McDermott, A., Zeger, S. L. and Samet, J. M., Fine particulate air pollution and hospital admission for cardiovascular and respiratory diseases, *J. Am. Med. Assoc.*, 295, 1127-1134(2006).

Frampton, M. W., Utell, M. J., Zareba, W., Oberdörster, G., Cox, C., Huang, L. S., Morrow, P. E., Lee, F. E., Chalupa, D., Frasier, L. M., Speers, D. M. and Stewart, J., Effects of exposure to ultrafine carbon particles in healthy subjects and subjects with asthma, *Res. Rep. Health Eff. Inst.*, 126, 1-47(2004).

Herzberg, G., Molecular Spectra and Molecular Structure, Part II Infrared & Raman Spectra of Polyatomic Molecules, D. Van Nostrand, NY. (1947).

Kampa, M. and Castanas, E., Human health effects of air pollution, *Environ. Pollut.*, 151, 362-367(2008).

Katsouyanni, K., Touloumi, G., Samolu, E., Petasakis, Y., Analitis, A., Le Tertre, A., Rossi, G., Zmirou, D., Ballester, F., Boumghar, A., Anderson, H.R., Wojtyniak, B., Paldy, A., Braustein, R., Pekkanen, J., Schindler, C. and Schwartz, J., Sensitivity analysis of various models of short-term effects of ambient particles on total mortality in 29 cities in APHEA2, In: Revised Analyses of Time-Series of Air Pollution and Health. *Special Report. Health Effects Institute, Boston, MA*, 157-164(2003).

Kim, E. and Hopke, P. K., Source characterization of ambient fine particles at multiple sites in the Seattle area, *Atmospheric Environment*, 42, 6047-6056(2008).

Kulshrestha, U. C., Nageswara Rao, T., Azhaguvel, S. and Kulshrestha, M. J., Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India, *Atmospheric Environment*, 38, 4421-4425(2004).

Kumar, Sudhanshu, Aggarwal, Shankar G., Gupta, Prabhat K., Kawamura and Kimitaka, Investigation of the tracers for plastic-enriched waste burning aerosols, *Atmospheric Environment*, 108, 49-58(2015).

Lary, D. J., Shallcross, D. E. and Toumi, R., *J. Geophys. Res.*, 104, 15929–15940(1999).

Mansouri, M. T. and Cauli, O., Motor alterations induced by chronic lead exposure, *Environ Toxicol. Pharmacol.*, 27, 307-313(2009).

Márquez-Ramírez, S. G., Delgado-Buenrostro, N. L., Chirino, Y. I., Iglesias, G. G. and López-Marure, R., Titanium dioxide nanoparticles inhibit proliferation and induce morphological changes and apoptosis in glial cells, *Toxicology*, 302(2-3), 146-156(2012). doi: 10.1016/j.tox.2012.09.005. Epub 2012 Oct 5.

Moreno, T., Querol, X., Alastuey, A., Minguillòn, M.C., Pey, J., Rodriguez, S., Mirò. J.V., Felis, C. and Gibbons, W., Recreational atmospheric pollution episodes: inhalable metalliferous particles from firework displays, *Atmospheric Environment*, 41, 913-922(2007).

Newton, M. C. and Warburton, P. A., ZnO tetrapod nanocrystals, *Materials Today*, 10(5), 50-54. (2007).

Oberdörster, G. and Yu, C. P., The carcinogenic potential of inhaled diesel exhaust – a particle effect?. *J. Aerosol Sci.*, 21, S397-S401(1990).

Ravindra, K., Mor, S. and Kaushik, C. P., Short-term variation in air quality associated with firework events: A case study, *Journal of Environment Monitoring*, 5, 260–264(2003).

Röösli, M., Theis, G., Künzli, N., Staehelin, J., Mathys, P., Oglesby, L., Camenzind, M. and Braun-Fahrländer, C., Temporal and spatial variation of the chemical composition of PM_{10} at urban and rural sites in the Basel area, Switzerland, *Atmospheric Environment*, 35, 3701-3713(2001).

Russell, M. S., Chemistry of Fireworks: RSC Paperback Series 2009, Royal Society of Chemistry, ISBN 0854041273(2009).

Sarkar, S., Khillare, P. S., Jyethi, D. S., Hasan, A. and Parween, M., Chemical speciation of respirable suspended particulate matter during a major firework festival in India, *J. Hazard. Mater.*, 184(1–3), 321–330(2010).

Silverstein, R. M., Bassler, G. C. and Morrill, T. C., Spectrometric identification of organic compounds, 3rd ed., John Wiley & Sons, NY. (1976).

Singh, D. P., Gadi, R., Mandal, T. K., Dixit, C. K., Singh, K., Saud, T., Singh, N. and Gupta, P. K., Study of temporal variation in ambient air quality during Diwali festival in India, *Environ. Monit. Assess.*, 169 (1–4), 1–13(2010).

Skocaj, M., Filipic, M., Petkovic, J. and Novak, S., Titanium dioxide in our everyday life; is it safe? RadiolOncol. 45(4), 227-247(2011). doi: 10.2478/v10019-011-0037-0. Epub2011 Nov 16.

Summerhays, J., Evaluation of risks from urban air-pollutants in the Southeast Chicago area, *J. Air Waste Manage. Assoc.* 41, 844–850(1991).

Fireworks, 2015; http://www.backcountryattitude.com/toxic_fireworks.html#ref_8; Last Access: 11 June 2015.

Stuart, B., Infrared Spectroscopy: Fundamentals and Applications, John Wiley & Sons, Ltd. ISBNs: 0-470-85427-8 (HB). (2004).

Toscano C. D. and Guilarte T. R., Lead neurotoxicity: from exposure to molecular effects, *Brain Res. Rev.*, 49, 529-554(2005).

Tronconi, E. and Groppi, G. A., Study on the thermal behavior of structured plate-type catalysts with metallic supports for gas/solid exothermic reactions, *Chem. Eng. Sci.*, 55, 6021-6036(2000).

Vecchi, R., Bernardoni, V., Cricchio, D., D'Alessandro, A., Fermo, P., Lucarelli, F., Nava, S., Piazzalunga, A. and Valli, G., The impact of fireworks on airborne particles, *Atmospheric Environment*, 42, 1121-1132(2008).

Vijayakumar, K. and Devara, P. C. S., Variations in aerosol optical and microphysical properties during an Indian festival observed with space-borne and ground-based observations, *Atmosfera.*, 25, 381-395(2012).

Wang, F. Z., Ye, Z. Z., Ma, D. W., Zhu, L. P. and Zhuge, F., Novel morphologies of ZnO Nanotetrapods, *Mater. Lett.*, 59, 560-563(2005).

Wilson, E. B., Decius, J. C. and Cross, P. C., Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra, McGraw-Hill(1955).